Further Results on Monte Carlo Equations of State

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The equation of state of three-dimensional hard spheres has been obtained by the Monte Carlo method. Some qualitative results for a system of two-dimensional molecules with Lennard-Jones interaction are also given, as well as a general discussion of the usefulness and limitations of the Monte Carlo method.

I. INTRODUCTION

THE purpose of this paper is to present some further results obtained by the Monte Carlo method.[1] Some qualitative results have been obtained for the system of two-dimensional molecules with Lennard-Jones interaction, and the equation of state for three-dimensional rigid spheres has been obtained.

II. QUALITATIVE RESULTS FOR THE SYSTEM OF TWO-DIMENSIONAL MOLECULES WITH LENNARD-JONES INTERACTION

Some work has been done on a two-dimensional system of fifty-six molecules with intermolecular potential:

$$V = (a/r^{12}) - (b/r^6). \qquad (1)$$

This work has been pursued far enough to obtain quantitative results, but does show some interesting qualitative features.

In particular, it was possible to observe the existence of the liquid-gas phase transition. Figure 1 is a typical plot of the positions of the fifty-six molecules at a temperature equal to one-half the well depth and for various values of A/A_0. Here, A is the area per molecule, and A_0 is the area per molecule in a close-packed lattice when the molecules are a distance apart, such that $V=0$.

Figure 1(a) $(A/A_0=1)$ represents a quite tightly packed configuration, hence the molecules are nearly in a regular lattice. (It should be borne in mind that due to our periodicity condition,[1] molecules near one edge of the square are neighbors of those near the opposite edge of the square.)

Figure 1(b) $(A/A_0=1.6)$ shows the molecules in a more expanded configuration in which they continue to fill up the square, although in a more irregular fashion. This configuration is close to the boiling point.

Figures 1(c) and 1(d) $(A/A_0=2$ and $A/A_0=2.52)$ represent still more expanded configurations. It will be observed that the molecules no longer continue to fill the square but that cavitation occurs. This presumably is the result of the phase transition—the area of the square becomes greater than the area of the liquid at its boiling point, and hence the liquid does not fill the

square. Since the density of the gas is very low, the gaseous phase appears as holes in the fluid.

The critical temperature phenomenon is also observed. Thus for high temperatures (the critical temperature appears very roughly equal to the well depth) cavitation no longer occurs.

The general shape of the isotherms is also in agreement with typical liquid-gas isotherms. However, it seems very difficult to obtain accurate quantitative results in the interesting transition regions.

There are several reasons for this:

(1) For our small sample of molecules the surface between fluid and bubbles is quite large and many molecules are on the surface. Thus, a large surface energy and pressure is introduced.

(2) The process of forming or destroying bubbles is a lengthy one, requiring many moves. Thus, it is difficult to reach equilibrium. In fact, over a considerable region of density a bubble will not be formed spontaneously but will persist once introduced into the fluid.

(3) For densities where the molecules are a distance apart corresponding to the potential minimum one must expect large fluctuations in the pressure. This comes about because the virial, rdV/dr, whose average value determines the pressure, varies strongly with the intermolecular distance while the energy and hence the probability factor $\exp(-E/kT)$ does not.

Thus, one cannot expect the Monte Carlo method to give great detail in the neighborhood of phase transitions, or certainly in the critical region, though it should be possible, for example, to determine the critical constants withinin 20 percent. In a one-phase region the Monte Carlo method should be feasible with an arbitrary intermolecular potential.

In view of the somewhat academic nature of the two-dimensional Lennard-Jones system, and the large amount of work which would be necessary to obtain quantitative results, no further work is contemplated on this case.

III. THREE-DIMENSIONAL RIGID SPHERES

Most of the work on three-dimensional rigid spheres was done with a sample of 256 molecules starting from a face-centered-cubic lattice. About twenty different densities were computed, and at each density each

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[1] Metropolis, Rosenbluth, Rosenbluth, Teller, and Teller, J. Chem. Phys. **21**, 1087 (1953). This paper discusses in detail the Monte Carlo method.

$$kT = \tfrac{1}{2} W \; \frac{A}{Ao} = 1$$
(a)

$$kT = \tfrac{1}{2} W \; \frac{A}{Ao} = 2$$
(c)

$$kT = \tfrac{1}{2} \; \frac{A}{Ao} = 1.6$$
(b)

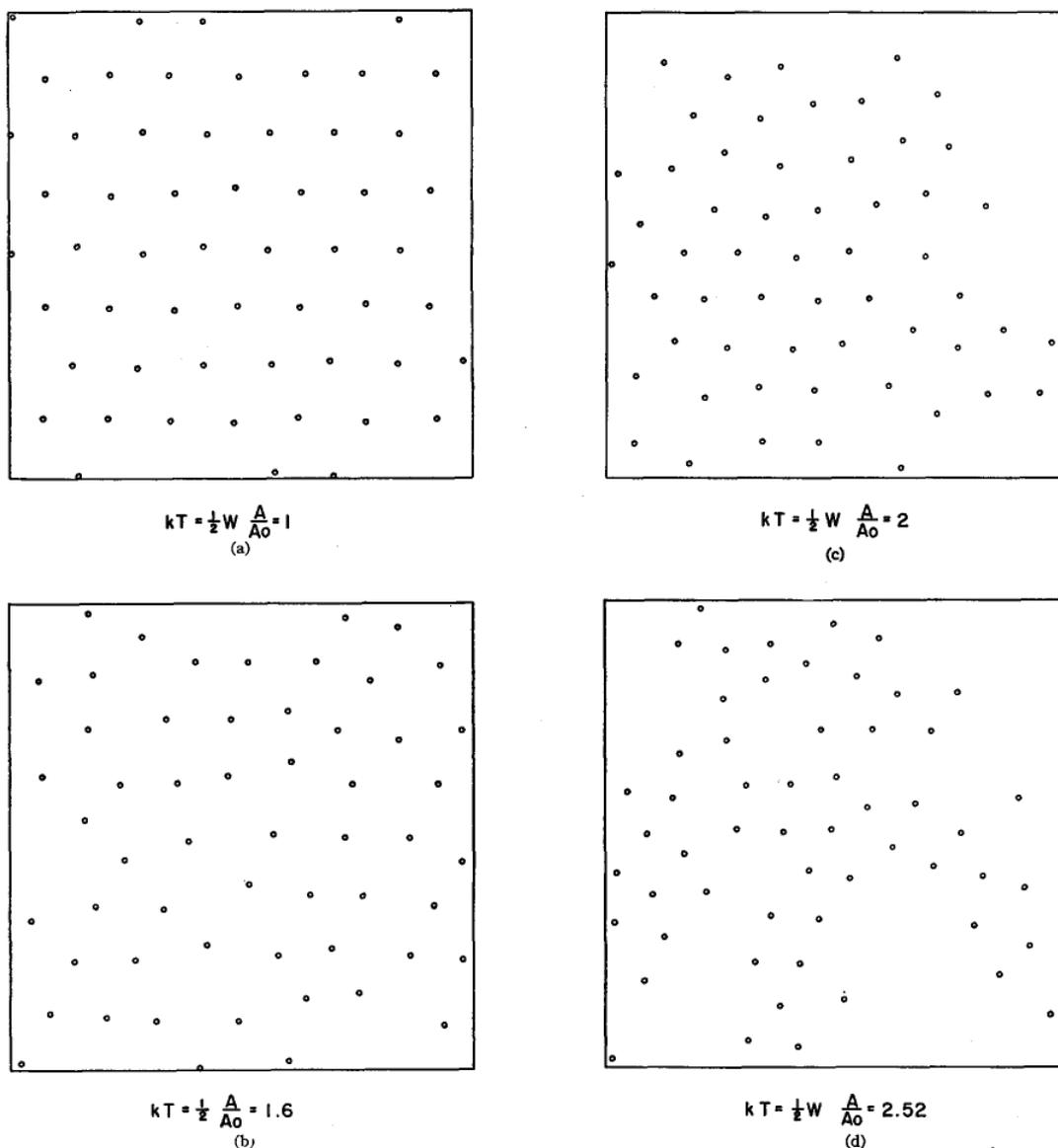$$kT = \tfrac{1}{2} W \; \frac{A}{Ao} = 2.52$$
(d)

FIG. 1. Typical plots of the positions of the 56 molecules for a two-dimensional system with a Lennard-Jones type interaction between pairs. The temperature is one-half the well depth. The ratio A, the area, to A_0, the area in a close packed system with the nearest neighbor distance such as to make the potential energy of nearest neighbors zero, is varied from 1 to 2.52 in the four diagrams.

molecule was moved about 100 times. This seemed quite sufficient for attaining equilibrium and reducing the statistical error below 5 percent. This program required about 150 hours of computing time on the Los Alamos MANIAC.

At each density the radial distribution function was obtained, and from it the pressure by means of the well known formula:

$$\frac{pV}{kT} - 1 = \frac{2\pi}{3} d_0{}^3 n(1). \qquad (2)$$

Here, d_0 is the molecular diameter, and $n(1)$ is the density of surrounding molecules at the surface of a molecule.

The equation of state is shown in Fig. 2 and Table I. Here $(pV/kT) - 1$ is plotted against $(V/V_0) - 1$. V is the volume per molecule, and V_0 the volume per molecule at the closest possible packing.

The equation of state agrees at low densities with the virial expansion as it should. At high densities it agrees fairly well with the free volume equation of state,[2]

[2] W. W. Wood, J. Chem. Phys. 20, 1334 (1952).

although not nearly as well as in the two-dimensional case. At high densities it disagrees strongly with the superposition theory of Kirkwood and Born-Green.[3] It should be noted that liquids have specific volumes about twice the close-packed specific volume of their "equivalent hard sphere repulsive cores," in which region the superposition theory does not deviate too much from our results.

Our equation of state shows no sign of a phase transition but a transition involving only a small change in volume, or a higher-order transition, would not have been observed, so this evidence is not conclusive.

Figure 3 shows some radial distribution functions. Here, n, the density of molecules surrounding a given molecule, is plotted as a function of the distance from the center of the given molecule. n is normalized so that it would equal one for a uniform distribution, and R is in units of the molecular diameter.

The curve at $V/V_0 = 1.145$ is quite crystalline in structure, showing the various layers of neighbors only slightly smeared out from their lattice positions. Another interesting feature of the distribution is that its maximum value does not occur at $R=1$ but rather at a slightly greater radius. This shift of the maximum does not occur in the two-dimensional case. Its occurrence in three dimensions is clearly a complex many-body phenomenon, and we have not been able to fully explain it.

At the highest compressions $[(V/V_0) < 1.1]$ the shape of the distribution function near $R=1$ is given approximately by

$$n = \frac{1}{V-V_0}\left\{ 1.1 - 0.15\left[\frac{R-1}{0.2\left(\dfrac{V}{V_0}-1\right)} - 1 \right]^2 \right\}. \quad (3)$$

As the density is decreased, the maximum becomes less pronounced and finally disappears at about $V/V_0 = 1.25$. At this point there is still a negative curvature to the distribution function at the origin but as the density is decreased still further to $V/V_0 = 1.5$, the curvature becomes positive.

The importance of the shape of the distribution function near the origin is, of course, that $pV/kT - 1$ is proportional to the molecular density at $R=1$ [see Eq. (2)]. Thus, the existence of the shifted maximum means a lowering of molecular density at $R=1$ and

hence a decrease in pressure. In fact, the behavior of the equation of state at high densities—its rise relative to the free volume equation of state as V is increased—can be ascribed to the manner in which the distribution function becomes successively more peaked at the origin.

The curve at $V/V_0 = 1.32$ still shows the crystalline structure though at this volume the peaks are quite smeared out.

The curve at $V/V_0 = 1.8$ looks quite different. Here the distinctive peaks have disappeared and one has a smoothly oscillating distribution function similar to those observed in liquids and to those obtained by the superposition theory.[3] The results differ from those of the superposition theory chiefly in that the magnitude of the oscillations is quite a bit larger for our radial distribution functions.

The transition between the solid and liquid type distribution functions seems to occur at about $V/V_0 = 1.5$. It occurs fairly gradually, however, so that we have not been able to say on this basis, either, whether a discontinuous phase transition takes place. It is interesting to note that $V/V_0 = 1.5$ is also where molecules were first able to slip past each other, another indication of lattice breakup. This fact facilitated the computation at high densities since here the original nearest neighbors of a molecule remained its nearest neighbors so that it was unnecessary to search through the lattice to determine the nearest neighbors of a molecule.

As has been mentioned earlier the indicated statistical error in the equation of state is about 5 percent. It is more difficult to estimate possible systematic errors. These might include the finite number of molecules and

TABLE I. Equation of state of three-dimensional hard spheres.

$\frac{V}{V_0}-1$	0.05	0.1	0.25	0.5	0.75	1	1.5	2	3
$\frac{pV}{kT}-1$	58	31	13.8	7.85	5.50	4.25	2.82	2.02	1.21

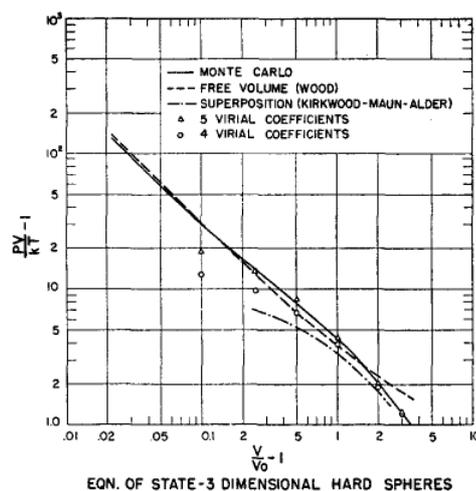[3] Kirkwood, Maun, and Alder, J. Chem. Phys. 18, 1040 (1950).

FIG. 2. A log-log plot of $(PV/kT) - 1$ versus $(V/V_0) - 1$ for hard spheres in three dimensions. Here V_0 is the volume per molecule at the closest possible packing. The solid line is the result of the Monte Carlo method as discussed in this paper; as compared to the free volume theory (dashed line), the superposition theory of Kirkwood (dot-dashed line), and to a 4 term (circles) and 5 term (triangles) virtual expansion.

the possibility that equilibrium was not reached, i.e., that what we calculated was a metastable configuration close to the initial lattice structure.

At low densities where only fairly small clusters are important our results should be good. At very high densities where the configuration must be nearly a regular lattice and where our periodicity condition should eliminate surface effects for a regular lattice our results should also be good. It is therefore in the intermediate density region where lattice breakup phenomena may be occurring that systematic errors might be large.

In order to check the effect of the finite number of molecules some runs were made using 32 and 108 molecules. These gave results within statistical error of the results obtained with 256.

In order to check the possibility that the system "remembered" its initial configuration some runs were made with the molecules initially crammed into one corner of the cell, instead of starting from a regular lattice. Here, too, the results were within statistical error. While these checks are not conclusive, they are an indication that systematic errors are not large.

Some runs were also made starting from a hexagonal-close-packed lattice. The pressures obtained were the same as for the face-centered cubic.
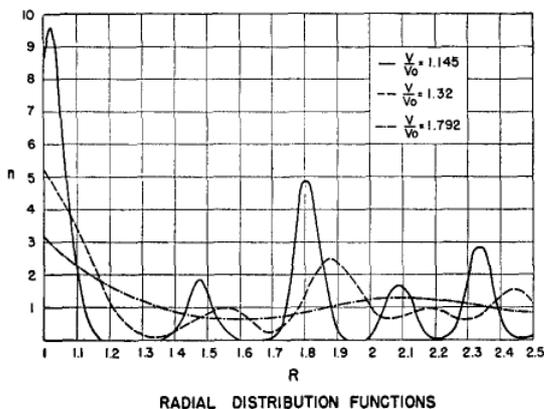

RADIAL DISTRIBUTION FUNCTIONS

FIG. 3. Radial distribution functions *versus* distance for three-dimensional hard spheres. Here n, the density of molecules surrounding a given molecule, is normalized to one for a uniform distribution. The distance R is given in units of the molecular diameter. Distribution functions for three volumes are shown.

The fifth virial coefficient was calculated by Monte Carlo evaluation of the cluster integrals.[1] One obtains thus:

$$\frac{pV}{kT}-1=2.962\left(\frac{V_0}{V}\right)+5.483\left(\frac{V_0}{V}\right)^2$$
$$+7.455\left(\frac{V_0}{V}\right)^3+8.9\left(\frac{V_0}{V}\right)^4.$$

The value of the coefficient of the last term, the one we calculated, has a statistical error of about 10 percent. Some values of $(pV/kT)-1$ as given by the four- and five-term virial expansions are shown on Fig. 2. It will be seen that the five-term expansion agrees very well with our equation of state at low densities. Moreover, the fact that the five-term expansion lies slightly above the equation of state at some densities indicates that some higher virial coefficients are negative.

IV. CONCLUSIONS

The equation of state for three-dimensional hard spheres casts doubt on the adequacy of the superposition approximation at high densities. The radial distribution functions obtained show a clear evolution with increasing volume from a crystalline structure to a liquid type structure with the transition being completed at about $V/V_0=1.5$. It is not possible to say, however, whether a discontinuous phase transition occurs.

Results obtained thus far lead us to feel strongly that the Monte Carlo method is a useful tool for solving statistical mechanical problems, although it does not appear to be feasible to obtain detailed results in transitions regions. The authors are now working on a modification of the method which will make it applicable to Bose-Einstein substances at zero temperature.